Indian J. Phys. **73A** (6), 793–799 (1999)

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IJP A
— an international journal

Evaluation of electronic dielectric constant of mixed crystals

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Received 9 February 1999, accepted 30 July 1999

Abstract : The values of refractive index n or electronic dielectric constant ε_∞ are calculated for mixed crystals of I–VII simple binary ($A^N B^{8-N}$ type) family. For such calculations the quantum ion dependent formulation is our first pedestal. The comparison is given for the values of electronic dielectric constant ε_∞ calculated from Claussius-Mossotti relation and quantum ion dependent formulation. An equivalence is found between the results obtained from classical theory and quantum ion dependent theory.

Keywords : Mixed crystals, electronic dielectric constant, simple binary and complex binary families.

PACS Nos. : 77.22.–d, 77.90.+k

The study of mixed crystals is a very interesting phenomenon because this study leads many fold applications in the industrial and technological fields. Some work has been completed in this direction considering the ionic alkali halides etc. [1–12], no general analysis has been given in the field of mixed crystals considering the simple binary and complex binary families.

In the present work, a general method for the evaluation of electronic dielectric constant ε_∞ is developed for mixed crystals of simple binary and complex binary families. In the considered family different systems of mixed crystals are classified in several ways, *viz.*,

(i) Those which are formed from substances having a common cation such as NaCl–NaBr (I–VII family).

(ii) Having a common anion such as CsCl–KCl (I–VII family).

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(iii) Having the two substances of same structure such as KCl–KBr (both in NaCl structure) or CsCl–CsBr (both in CsCl structure), I–VII family.

(iv) Having the two substances of different structures such as CsCl–RbCl and CsCl–KCl (I–VII family).

In the present work, the first four solid solutions (NaCl–NaBr, KCl–KBr, KBr–KI and CsCl–CsBr) are with common cation where as last two (CsCl–RbCl and CsCl–KCl) with common anion.

The correlation [13] between electronic dielectric constant ε_∞ and interionic separation R is given by

$$\varepsilon_\infty = 1 + B R^s \tag{1}$$

where B is ionic characteristic constant and s is family characteristic constant. Equation (1) is a quantum ion dependent formulation and is found to be valid for all the simple binary families ($A^N B^{8-N}$ type) and also for complex binary families (like AB_2, A_2B, A_3B and A_3B_2 types). In the category of simple binary families we have I–VII ($N = 1$), II–VI ($N = 2$) and III–V ($N = 3$). The representative analysis is given for I–VII family. The characteristic constants and interionic separations [1] are given in Table 1 and Table 2, respectively.

Table 1. Characteristic constants (s-family characteristic constant and B-ion characteristic constant).

Family	Substances	Cation	s	B
	LiF, LiCl, LiBr, LiI,	Li	3.00	-
	NaF, NaCl, NaBr, NaI	Na	3.00	0 0580
I–VII	KF, KCl, KBr, KI,	K	3.00	0.0375
	RbF, RbCl, RbBr, RbI,	Rb	3.00	0.0331
	CsF, CsCl, CsBr, CsI	Cs	3.00	0 0357

Table 2. The values of interionic separation $R(10^{-10}\text{m})$ for pure crystals of I–VII family.

Crystals	R
NaCl	2.820
NaBr	2.989
KCl	3 147
KBr	3.300
KI	3.533
RbCl	3.291
CsCl	3.571
CsBr	3.720

In common cation systems of mixed crystals we will use the common ionic characteristic constant, for example, in case of NaCl–NaBr mixed crystals $B = 0.0580$ (because the I–VII family shows cation dependence). But in case of CsCl–RbCl (common anion) mixed crystals average ion characteristic constant is used for example in case of CsCl–RbCl mixed crystals,

$$B = \frac{1}{2}(0.0357 + 0.0331)$$

Values of interionic separation for mixed systems are calculated from the relation,

$$R^n = \lambda_1 R_1^n + \lambda_2 R_2^n$$

where λ_1 and λ_2 are the proportions of component crystals mixed together, R_1 and R_2 are the interionic separations for pure crystals. It has been found that with $n = 3$, above relation produces the best fit to the available experimental data on mixed crystals [5,7]. Thus, above relation reduces to,

$$R^3 = \lambda_1 R_1^3 + \lambda_2 R_2^3 \tag{2}$$

The values of electronic dielectric constant calculated with the help of quantum ion dependent theory (equation-1) are reported in Tables 3a, 3b, 3c and 3d; 4a and 4b along

Table 3(a). Values of interionic separation $R(10^{-10}$ m) and electronic dielectric constant ε_∞ of mixed crystals with common cation, (a) calculated from present study and (b) from the Claussius-Mossotti formula for I–VII simple binary family.

NaCl–NaBr (% NaBr)	R	ε_∞ (a)	ε_∞ (b)
0	2.820	2.30	2.33
10	2.839	2.33	2.36
17	2.850	2.34	2.38
26	2.866	2.39	2.41
36	2.883	2.39	2.43
46	2.900	2.41	2.46
55	2.915	2.44	2.49
70	2.940	2.47	2.53
83	2.962	2.51	2.56
100	2.989	2.55	2.60

with the values of interionic separations for mixed systems. For comparison column (b) is also given where the values [1,10] of electronic dielectric constant are given calculated from Claussius-Mossotti relation,

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{4\pi}{3}\frac{\alpha}{V} \tag{3}$$

here α and V are the electronic polarizability and volume per ion pair, respectively.

Table 3(b). Values of interionic separation $R(10^{-10}$ m) and electronic dielectric constant ε_∞ of mixed crystals with common cation, (a) calculated from present study and (b) from the Claussius-Mossotti formula for I–VII simple binary family.

KCl–KBr (% KBr)	R	ε_∞ (a)	ε_∞ (b)
0	3.147	2.17	2.17
6	3.156	2.18	2.19
13	3.167	2.19	2.20
38	3.206	2.24	2.25
54	3.230	2.26	2.28
61	3.241	2.28	2.29
71	3.256	2.30	2 31
85	3.276	2.32	2.33
100	3.298	2 35	2 36

Table 3(c). Values of interionic separation $R(10^{-10}$ m) and electronic dielectric constant ε_∞ of mixed crystals with common cation, (a) calculated from present study and (b) from the Claussius-Mossotti formula for I–VII simple binary family.

KBr–KI (% KI)	R	ε_∞ (a)	ε_∞ (b)
0	3.298	2.35	2.36
10	3.322	2.38	2.39
15	3.334	2.39	2.41
22	3.350	2.41	2.43
29	3.336	2.43	2 45
40	3.392	2.46	2.48
48	3.410	2.49	2.51
60	3.437	2.52	2.54
80	3.490	2.59	2.60
90	3.502	2.64	2.62
100	3.533	2.65	2.65

Table 3(d). Values of interionic separation $R(10^{-10}$ m) and electronic dielectric constant ε_∞ of mixed crystals with common cation, (a) calculated from present study and (b) from the Claussius-Mossotti formula for I–VII simple binary family.

CsCl–CsBr (% CsBr)	R	ε_∞ (a)	(b)
0	3.571	2.63	2.63
5	3.578	2.64	2.64
10	3.586	2.65	2.65
20	3.601	2.67	2.66
30	3.616	2.69	2.68
40	3.632	2.71	2.69
50	3.647	2.73	2.71
60	3.661	2.75	2 72
70	3.676	2.77	2.74
80	3.681	2.78	2.75
90	3.705	2.82	2.77
100	3 720	2.84	2 78

Table 4(a). Values of interionic separation $R(10^{-10}$ m) and electronic dielectric constant ε_∞ of mixed crystals with common anion, (a) calculated from present study and (b) from the Claussius-Mossotti formula for I–VII simple binary family.

CsCl–KCl (% KCl)	R	ε_∞ (a)	ε_∞ (b)
0	3.571	2.67	2 63
2.5	3.562	2.65	2.62
5	3.552	2 64	2.61
10	3.533	2.61	2.58
20	3.494	2.56	2.54
25	3.474	2.55	2.52
35	3.434	2 48	2.47
45	3.393	2.43	2.42
55	3.351	2.38	2.38
65	3.307	2.32	2.33
75	3.263	2.27	2.29
85	3.217	2.22	2.24
100	3.147	2.14	2.17

Table 4(b). Values of interionic separation $R(10^{-10}$ m) and electronic dielectric constant ε_∞ of mixed crystals with common anion, (a) calculated from present study and (b) from the Claussius-Mossotti formula for I–VII simple binary family.

CsCl–RbCl (% RbCl)	R	ε_∞ (a)	ε_∞ (b)
0	3.571	2.57	2.63
5	3.558	2.58	2.60
7.5	3.551	2.54	2.59
10	3.544	2.53	2.58
25	3.505	2.48	2.51
30	3.491	2.46	2.48
32.5	3.484	2.46	2.48
50	3.436	2.40	2.39
60	3.408	2.36	2.35
70	3.379	2.33	2.30
80	3.350	2.29	2.26
90	3.321	2.26	2.22
100	3.291	2.23	2.18

Considering I–VII simple binary family, the values of electronic dielectric constant are calculated for mixed cyrstals, classified on the basis of common anion or common cation. The same method will be applicable for the other simple binary and complex binary families. The predictions in case of mixed systems will be useful in understanding structural and dielectric properties of ionic and covalent systems in different families.

It is found that the values of electronic dielectric constant ε_∞ calculated from the equation (1) which has the quantum basis, agree closely with the corresponding values derived from classical model due to Claussius and Mossotti (Tables 3, 4). Such a comparison of results obtained from two different approaches increases the reliability of the values of electronic dielectric constant. The mixed systems CsCl–RbCl and CsCl–KCl are of particular importance due to structural phase transition [11]. The mixed system CsCl–RbCl undergoes a structural phase transition from CsCl to NaCl structure for RbCl exceeding 50%, similar transition is observed for CsCl–KCl mixed crystals when KCl is more than 25%.

Acknowledgment

The authors are thankful to Prof. Jai Shanker, Basic Science Institute, Khandari, Agra, for useful suggestions.

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